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Procedia Chemistry 17 (2015) 153 – 156

Procedia Chemistry

3rd International Seminar on Chemistry 2014

# Optimization in Mediated Electrochemical Oxidation Using Cobalt Sulfate as a Mediator

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**Abstract**

Optimization of the Mediated Electrochemical Oxidation (MEO) for destructing a dissolved organic compound has been studied. The experiment was carried out in a 100 mL electrolytic cell equipped with a rotameter, an outlet tube of "tetradent" designs, a collecting tube, a stabilized DC power supply, and electrodes which were fabricated from platinum foil. It has been found that optimum efficiency of destruction of glucose as a model of compound could be achieved by using cobalt sulfate as a mediator, at its optimum concentration of 0.43 M, in a 2 M sulfuric acid solution, for a glucose concentration of 0.2 M. The time required for optimum destruction efficiency was 2 hours.

*Keywords:* Mediated Electrochemical Oxidation, cobalt sulphate, glucose, optimization.

## 1. Introduction

Optimization of the concentration of cobalt sulphate mediator used in the predicted electrochemical process will reduce the onset time for turbidity in the collecting solution due to absorption of the carbon dioxide gas produced. It will also reduce the time required for complete mineralization of glucose. Cobalt sulphate has been used as a redox mediator in the oxidation of dissolved organic compounds to produce carbon dioxide gas and other simple organic compounds as by products. The cobalt compound was selected as a mediator considering its good oxidative properties, which can be inferred from the following facts and data. For example, cobalt has two common oxidation states, 2 and 3, $Co^{3+}$ is a stronger oxidant than $Fe^{3+}$, $Co^{2+}$ is stable in aqueous solution, $E^o$ for $Co^{3+}/Co^{2+}$ is + 1.93 V, whereas $E^o$ for the $Co^{2+}/Co$ system is – 0.28 V[1]. Another important reason for the use of cobalt sulphate as a mediator is its non-toxicity[2].

A metallic redox couple $Co^{2+}/Co^{3+}$ is used on the basis of its oxidative ability for indirect electro-oxidation processes. Cations with higher charge or oxidation state react with pollutants or other organic substrates (dissolved organic compounds) yielding the reduced form of the ion. This is in turn anodically oxidized to regenerate the oxidizing cation. This loop increases efficiency for destruction of contaminants[3].

The spectacular action of cobalt sulphate as a mediator can be exploited for the removal of organic componen of mixed (hazardous and radioactive) waste. In ambient temperature aqueous-phase processes, the strongest oxidizing agents serve as the most efficient mediators, and halide-tolerant $Co^{3+}$ requires no electrode separator. Sulphuric acid has been used as supporting electrolyte[4].

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## 2. Materials and method

### 2.1. Reagents and Apparatus

Glucose solutions investigated in this study were prepared using analytical reagent grade chemicals and deionised water. Cobalt sulphate, hydrochloric acid, phenolphthalein, barium hydroxide, and sulfuric acid were of the highest available grade. The experiments were carried out in a 100 mL double walled electrolytic cell. A rotameter flow meter[5], outlet tubes unmodified and



Peer-review under responsibility of Department of Chemistry, Faculty of Mathematics and Natural Sciences, Padjadjaran University
doi:10.1016/j.proche.2015.12.103

"tetradent" designs, collecting solution of 500 mL volume, and a stabilized power supply DC with a maximum output of 24 V, and a current-voltage monitor. Both anode and cathode were fabricated from platinum foil to have the geometry: 3.2 mm (height), 3.2 mm (width), 0.05 mm (thickness), and they were placed vertically and parallel to each other in the electrolytic cell with the distance 2.2 mm. Block diagram of the apparatus is shown in Figure 1. The system was constructed of local and commercially available parts for the electrolytic cell, outlet tube, collecting solution tube, glass delivery tube, clamps, stabilized DC power supply (a Topward Electric Instruments Co, Ltd model TPS 2000, monitoring voltage and current), flowmeter (Fisher and Porter model 10A6130), and high purity nitrogen gas supply (Bo gases) including gas flow regulator, and timer.

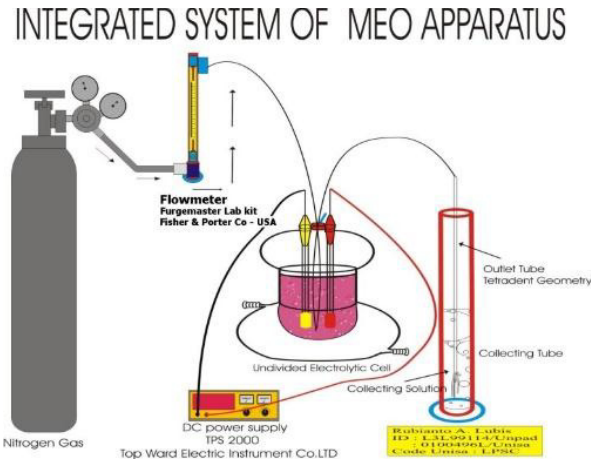


Fig. 1. Schematic of the integrated system of MEO apparatus

*2.2. Experimental Method*

The experiment were carried out as in the previous report. The data treatment used a simple regression equation $Y = bX + a$ with 5 (five) different concentration levels.

*2.2. Methods of Analysis*

The carbon dioxide generated by the substrate was determined by back titration of the collector solution with standart hydrochloric acid solution after settling and separating the precipitate. The onset of turbidity was the observed visually. Mineralisation of the dissolved glucose to carbon dioxide was monitored via the formation of barium carbonate precipitate in the colleting solution. Carbon dioxide quantity was determined by back titration of the barium hydroxide with standard hydrochloric acid solution after settling and separation of the precipitate.

*2.3. Realization of the optimization of the concentration of cobalt sulfate-mediator*

The experimental procedure carried out on the blank solution was repeated at various concentrations of cobalt sulphate, Electrolysis was carried out for 2 hours in each instance. Oxidation of the blank solution was monitored by visual observation of colour change as a function of time. It has accrued colour changes to the cobalt sulphate mediator solution during 15 minute operation from pink to red black (power on) and red black to light red (power off). A blank solution was used for investigation of the characteristics of the electrodes and cobalt sulphate-mediator solution, relevant colour changes are documented as a function of time with the power on and during the recovery period after switching it off, same metallic cobalt was deposited at the surface of the platinum cathode after 10 minutes of operation. After ten minute operation of electrolysis, same metallic cobalt was detested at the surface of the platinum cathode as seen in Figure 2 and Figure 3, respectively.

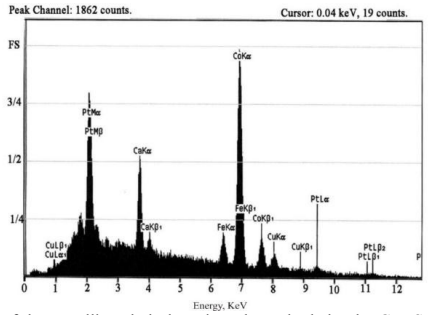


Fig. 2. The result of the examination of the metallic cobalt deposit at the cathode by the CamScan 44FE Scanning Electron Microscope using the attached Si(Li) Energy Dispersive X-ray Spectrometer at 20keV beam energy, one microampere

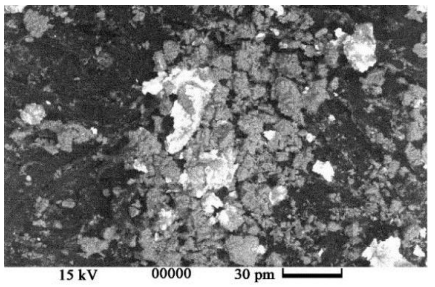


Fig. 3. SEM micrograph of a metallic cobalt deposit at the cathode using the CamScan 44FE Energy Dispersive X-ray Spectrometer

This procedure was repeated with various concentrations of cobalt sulphate, and then with a glucose concentration of 0.02 M. The collecting tube was charged with barium hydroxide-collecting solution (300 mLs, 0.1 M). Electrolysis was carried out for 2 hours in each instance. For the mediator concentration optimisation study the four working solutions in the electrolytic cell were made up from the following: mediator (I M cobalt sulphate) 1 - 20 mL, deionised water (19 – 0 mL) 2 M sulphuric acid 20 mL and glucose test solution (6 mL) this yielded glucose concentrations from 0.02 to 0.43 M. The product gas, carbon dioxide, and the carrier nitrogen gas, passed into the collecting solution. The flow rate of nitrogen gas was manually maintained at 1 mL/min during the process. (Table 1)

Table 1. Data for cobalt sulphate-mediator concentration optimization study

| Volume (mL) | | | | Concentration of the working solution of cobalt sulphate - mediator |
|---|---|---|---|---|
| 2 M $H_2SO_4$ | 1 M $CoSO_4$ | $H_2O$ | 0.2 M Glucose test solution | |
| 20 | 1 | 19 | 6 | 0.02 |
| 20 | 5 | 15 | 6 | 0.11 |
| 20 | 10 | 10 | 6 | 0.22 |
| 20 | 20 | - | 6 | 0.43 |

The effect of cobalt sulphate-mediator concentration on the time for first appearance of turbidity is shown in Table 2 and Fig. 4; this is a plot of time (minutes) vs. $\log_{10}$ concentration of cobalt (II) sulphate-mediator (M). Figure 5, is a plot of 1/time (min) vs. the concentration of cobalt sulphate-mediator (M). A straight line with a negative slope of -5.17 and a positive intercept of 31.2 and $R^2 = 0.9192$ was obtained. The equation is $y = 31.2 - 5.17x$. A linear relationship ($y = a + b\,x$) was observed where a is -0.258, b is 7.391, and $r_{xy} = 0.967$. The equation is: $y = -0.258 + 7.391\,x$. Here x is concentration of mediator (M), and y is 1/time (min) and $R_{xy}$ is a regression coefficient of the Pearson model correlation between concentration of cobalt sulphate-mediator and the reciprocal of the initial time of appearance of turbidity.

Table 2. Results of the determination of the optimum concentration cobalt sulphate toward glucose with barium hydroxide as collecting solution. Electrolysis conditions are E = 6V DC, 3A, unmodified outlet tube.

| Various Concentrations of Cobalt sulfate-mediator | Time for first appearance of turbidity (minutes) |
|---|---|
| 0.02 | 27.6 |
| 0.11 | 18.0 |
| 0.22 | 16.7 |
| 0.43 | 10.8 |

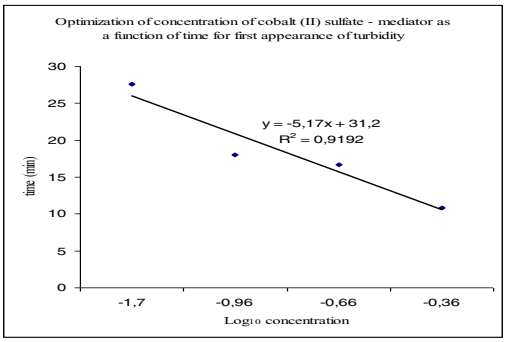


Fig. 4. Variation of time for first appearance of turbidity plotted as a function of $\log_{10}$ concentration

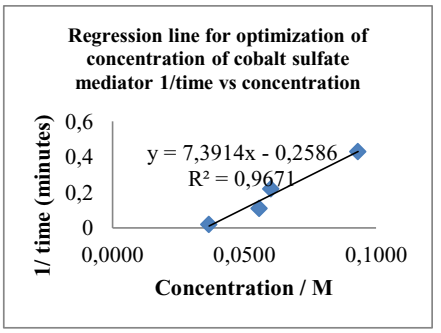


Fig. 5. Alternative representation of the first appearance of turbidity data for glucose

The strongest effect of mediator concentration was observed using 0.43 M. It was decided not to go above this level in case it posed any problems in the effective collection and detection of the evolved carbon dioxide. The reaction involved is as follows:

$$C_6H_{12}O_6 + 6\ H_2O + 24\ Co^{3+} \rightarrow 6\ CO_2 + 24\ H^+ + 24\ Co^{2+} + 24e$$

From Table 1, glucose is only very slowly oxidized at the 0.02 M mediator concentration. The reaction rate increases significantly as the mediator concentration is increased.

## Conclusions

As shown by the experimental data for oxidation of glucose in Table 2, increasing the cobalt sulphate-mediator concentration from 0.02 to 0.43 M, reduces the time for appearance of turbidity in the collector solution from 27.6 to 10.8 min. The concentration of 0.43 M cobalt sulphate-mediator (and 2 M sulphuric acid) was selected for all subsequent work. The shorter electrolysis process times achieved correlate with greater efficiency of degradation of the organic compound. Mediator concentration, acid concentration, current employed, and time were the key parameters.

## Acknowledgements

We thank the Directorate General of Higher Education, Ministry of Education and Culture, Indonesia for their financial support of the project.

## References

1. Kirk-Othmer, *Encyclopedia of Chemical Technology*. 1993. John Wiley & Sons. Inc, New York.
2. Burns, D.T., Townshend, A., and Carter, A.H. 1981. *Inorganic Reaction Chemistry*, *Vol 2 Part B*. West Sussex-England: Ellis Horwood Ltd.
3. Brillas, E., and Sauleda, R, Cassado, J. 1998. *Degradation of 4-hloro phenol by Anodic Oxidation, Electro-Fenton, Photoelectro-Fenton, and Peroxi-Coagulation Processes:* J. Electrochem. Soc, 145, 3.
4. Farmer. J.C, Wang. F.T, Hickman. R.G, Lewis. P.R. 1996. *Mediated Electrochemical Oxidation of Organic Waste without Electrode Separators*. US. Pat 5,516,972. May 14, 1996. The Regents of University of California, (Oakland. CA),
5. Freemantle, M. 1995. *Chemistry in Action*, Macmillan Press Ltd, London.
6. Sharpe. A. G. 1992. *Inorganic Chemistry*, Longman, Singapore.